

Cite this: *Org. Chem. Res.* **2022**, Vol. 8, 113-119.

DOI: 10.22036/org.chem.2024.437569.1320

An Introduction to the Synthesis of High-energy Materials

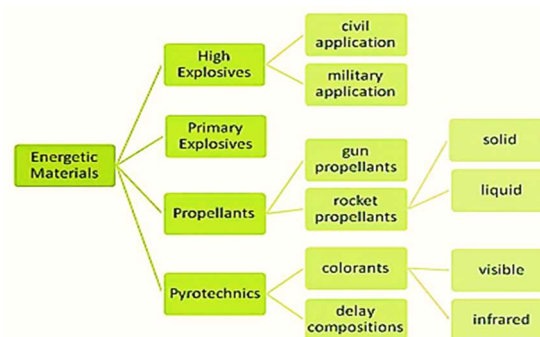
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Received: January 25, 2024; Accepted: February 20, 2024

Minireviews-Spotlight: This feature focuses on a reagent and subject chosen by a postgraduate, highlighting the hot topic subjects or uses and preparation of the reagent in current research.

Abstract: Energy materials include substances used for the production, conversion, storage, and transmission of energy. Explosives as a part of 'energetic materials' are substances of which the internally stored huge chemical energy is liberated with a (self-sustaining) rapid and violent chemical reaction initiated with an outer stimulant; energetic materials include explosives, propellants and pyrotechnics. Certain items such as natural fuels (fossil and synthetic fuels) burned in thermal power plants and motor vehicles, in conjunction with nuclear fuels (reacted in nuclear power plants) capable of emitting radioactive rays (alpha, beta and gamma rays) and undergoing nuclear fission or fusion reactions have been deliberately excluded from this review. Additionally, either metals conducting heat or electricity with a reasonable resistance or superconductor materials transmitting electricity with practically no resistance (i.e. without loss) do not take place in this work. Therefore, energy materials have been tailored to include batteries and accumulators, fuel cells, photovoltaic and optoelectronic materials, and thermoelectric and piezoelectric materials, that basically convert and store chemical energy, radiation, heat, and mechanical energy in the form of electrical energy (or vice versa). This review aims to discuss the definitions, backgrounds, working principles and applications of these systems to serve daily life. In addition to these, particular emphasis has been made on energetic materials, especially on explosives capable of liberating high amounts of heat and pressure in a rapid self-sustaining exothermic degradation reaction when appropriately stimulated.



Keywords: Fuel cells, Optoelectronic materials, Thermoelectric materials, Explosives, Propellants, Pyrotechnics, Energetic materials

1. Introduction

Nitrogen oxides (NO_x) such as NO , NOCl , NO_2X ($\text{X}=\text{Py}$, RO^- , RCO_2^- , Cl^- , BF_4^- , PF_6^-), N_2O_3 , N_2O_5 , and $\text{NO}_2/\text{N}_2\text{O}_4$, have been found a wide range of applications in organic synthesis, both in industry and in research laboratories.¹⁻³ Amongst these, $\text{NO}_2/\text{N}_2\text{O}_4$ exhibits important advantages as a versatile reagent over the others. Such advantages include its application as a multifunctional agent (nitration, nitrosation, and oxidation agent), as well as its being a powerful reagent and cost-effective. Although it is an ancient reagent of which the chemistry is well known, recent findings have revealed some crucial advances in terms of ease of handling. In this regard, N_2O_4 organic complexes such as 18-crown-6 ether/ N_2O_4 ^{4,5} and heterogeneous systems such as activated charcoal/ N_2O_4 ⁶ were explored as useful reagents that solve numerous handling problems and serve to increase the selectivity of $\text{N}_2\text{O}_4/\text{NO}_2$ in organic reactions. Metal nitrate/ N_2O_4 adducts, $\text{M}(\text{NO}_3)_x \cdot y\text{N}_2\text{O}_4$, in which N_2O_4 molecules are trapped in the metal nitrate lattice, were synthesized from the reaction of N_2O_4 and the corresponding

metal salts.⁷ Since liquid N_2O_4 evaporates at 21.15 °C under atmospheric pressure, $\text{M}(\text{NO}_3)_x \cdot y\text{N}_2\text{O}_4$ is a very convenient and thermally stable source of N_2O_4 . To increase the rate and selectivity of NO_2 in the laboratory, some modifications have been introduced for the reaction conditions such as the involvement of O_3 , O_2 , or zeolites, etc., and the use of ionic liquids. Nitration of arenes is an interesting process, not only for the application of nitroarenes as explosives but also due to the versatile use of nitroarenes as intermediates in various important functional group transformations. Although a recent book on such methods has been published, this section will focus on some new applications.⁸ A high-energy material (HEM) is a substance that can undergo a rapid chemical reaction when stimulated. The stimulus can be in the form of a spark, friction, flame, impact, shock, heat, or light energy. The reaction is very rapid and can result in very high pressures and the production of lighter gaseous products. While the production of gaseous products is of vital importance for space applications where the thrust is needed, the high pressures are useful for military applications. HEMs are also known by

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another name-explosive.⁹⁻¹⁰ Jai Prakash Agrawal said "...To camouflage research on explosives, propellants, and pyrotechnics, a new term 'high energy materials (HEMs)' was coined by the explosives community for them. Thus, all explosives, propellants, and pyrotechnics can be referred to as high-energy materials or energetic materials (EMs).¹¹ In other words; the other names of HEMs/EMs are explosives, propellants, and pyrotechnics depending on their formulations and intended use. Nowadays, the term HEMs/EMs is generally used for any material that can attain a highly energetic state mostly by chemical reactions these materials are divided into two groups based on expansion after explosion: low explosives and high explosives. Low explosives include black powder, smokeless gunpowder, and low-vulnerability ammunition.¹² High explosives are further divided into three subgroups primary, secondary, and tertiary explosives. Primary explosives include compounds like lead azide and hexamethylene triperoxide diamine, and secondary explosives comprise triacetone triperoxide, royal demolition explosive, C4, high melting explosive, dynamite, and trinitrotoluene (TNT). Tertiary explosives include ammonium nitrate aluminum powder and ammonium nitrate fuel oil.¹³⁻¹⁵ given their extensive use in civilian applications; HEMs are also categorized based on their use as military and civilian explosives. The ability to sense these materials from a distance is an important requirement. Given the nature of the material and the needs of the application, remote and standoff detection is an important criterion for choosing an appropriate method of detection.¹⁶ Most of the secondary explosives have carbon, nitrogen, oxygen, and hydrogen as the elemental building blocks. Any organic matter is a possible interferent as they

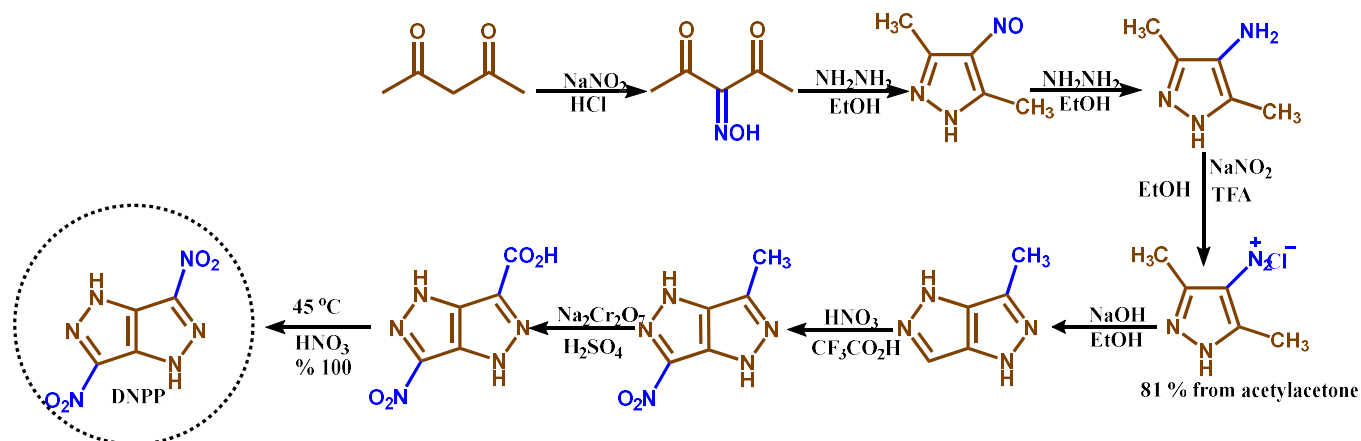
have similar constituents. The presence of oxygen and nitrogen in the atmosphere is another challenge as detection is supposed to be achieved in the open atmosphere.¹⁷⁻¹⁹

2. Synthesis of energetic materials

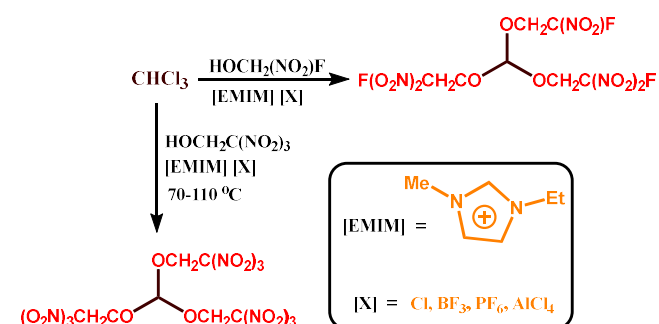
Recently, at Lawrence Livermore National Laboratory (LLNL), they have used molecular modeling and explosive performance prediction codes to guide the synthesis of new energetic materials based on the pyrazolo[4,3-c]pyrazole ring system with energies greater than HMX. The most significant improvement was the combination of the decarboxylation and nitration steps into a single nitrative decarboxylation step. Therefore, 3-carboxy-6-nitro-pyrazol [4,3-c]pyrazole was treated with 98% HNO₃ at 45 °C to give DNPP in 70% yield. The overall yield of DNPP from acetylacetone was 21%, which represents a significant increase from the Shevelev synthesis (Scheme 1).²⁰

Room temperature ionic liquids such as, e.g., ethyl methyl imidazolium, are promising reaction media for a variety of chemical processes. They are widely available, fire resistant, recyclable, and have limited vapor pressure, allowing efficient recovery of organic products. The energetic materials 2,2,2-trinitroethyl and 2-fluoro-2,2-dinitroethyl compounds are used as ingredients in explosive compositions, propellant formulations, and gas-generating compositions. Sheremetev and Yudin [54] reported the synthesis of 2-R-2,2-dinitroethanol orthoesters using room-temperature ionic liquids (Figures 9 and 10, EMIM is ethyl methyl imidazolium).

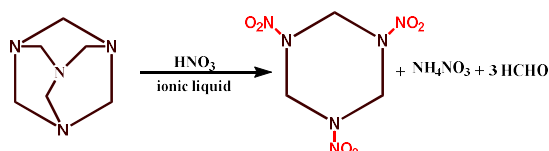
(Scheme 2, 3).²¹⁻²²



Scheme 1. Synthesis of DNPP

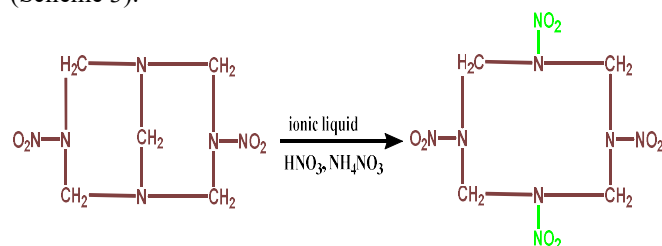


Scheme 2. Structure of room temperature ionic liquid and Synthesis of 2-R-2,2-dinitroethanol orthoesters room temperature ionic liquids



Scheme 3. Synthesis of 1,3,5-trinitro-1,3,5-triazinane room temperature ionic liquids

Luo *et al.* described the Synthesis of HMX via nitrolysis of DPT catalyzed by acidic ionic liquids. Some substrates such as TAT and DADN can afford HMX in high yield but need three or more steps. This approach is not economical or environmentally friendly. He *et al.* investigated the nitrolysis of DPT to synthesize HMX with ionic liquids as catalysts (Scheme 3).²³



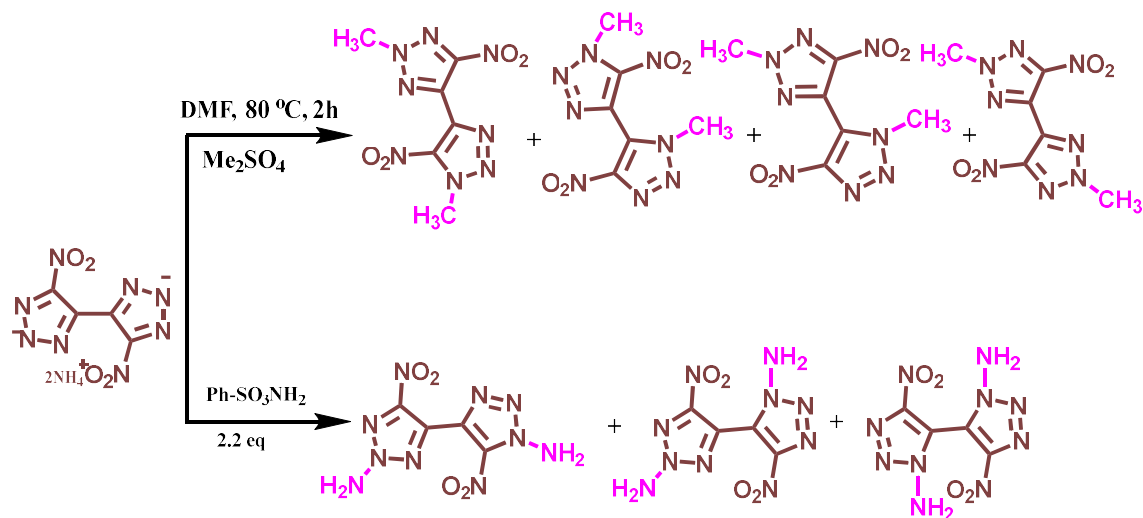
Scheme 3. Synthesis of HMX via nitrolysis of DPT catalyzed by acidic ionic liquids

Using a variety of functionalization strategies, derivatives of 4,4'-bis (5-nitro-1,2,3-2H-triazole) were designed, synthesized, and characterized. The isomers were separated, their structures were confirmed with single-crystal X-ray analysis, and their properties were determined by differential scanning calorimetry, density, and impact sensitivity, heat of formation, and detonation velocity and pressure (calculated by EXPLO5 V6.01). Those materials were found to exhibit superior detonation performance when compared with the other fully carbon-nitrated bis(azoles) (Scheme 4).²⁴

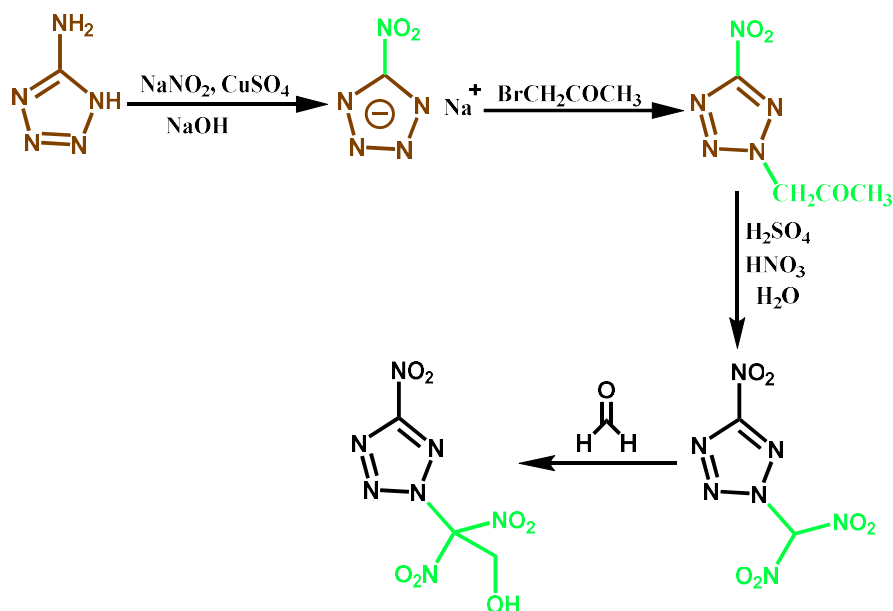
Luo *et al.* described design and synthesis of energetic materials toward high density and positive oxygen balance by *N*-dinitromethyl functionalization of nitroazoles. a new *N*-dinitromethyl functionalized strategy, *N*-dinitromethyl, was utilized for the synthesis of nitroazoles-based energetic materials, giving rise to a new family of highly dense and oxygen-rich energetic materials (Scheme 5).²⁴

Zolfigol *et al.* using [PVI-SO₃H]NO₃ as a new polymer Nitrate agents with ion tags succeeded in synthesizing new energetic compounds. (Scheme 6).²⁵⁻²⁷

Poly (vinyl imidazole) sulfonic acid nitrate [PVI-SO₃H]NO₃ was synthesized and fully characterized. Then, [PVI-SO₃H]NO₃ was applied for the preparation of energetic materials such as 1,1-diamino-2,2-nitroethane (FOX-7), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT). The major advantages of the presented methodology are mild, facile workup, high yields, and short reaction times. [PVI-SO₃H]NO₃ is a suitable nitrating agent for in situ generation of NO₂ and without using any co-catalysts of the described nitrating agent.

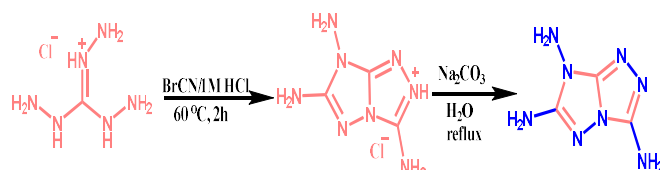


Scheme 4. Derivatives of 5-nitro-1,2,3-2H-triazole



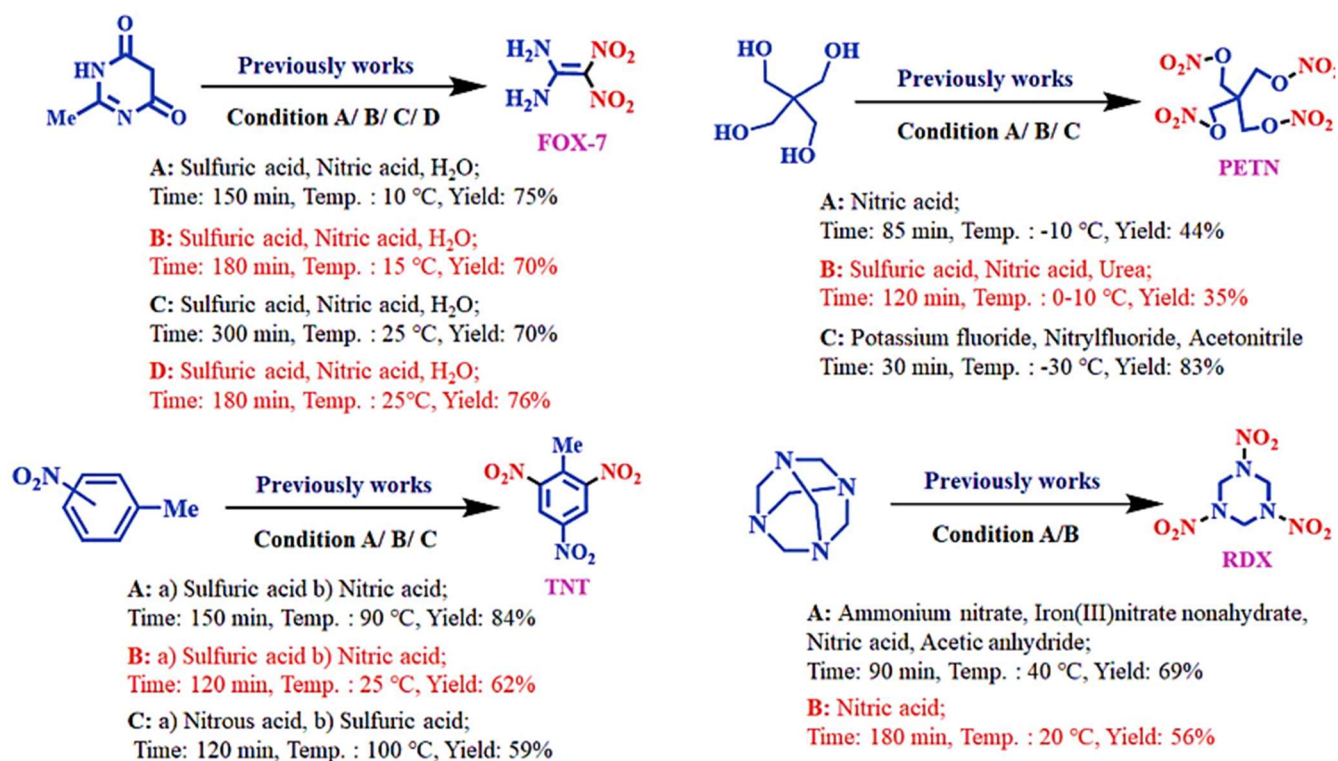
Scheme 5. Synthesis of N-dinitromethyl functionalized nitroazoles and their derivatives

Gao et al succeeded by using different catalysts under different temperature conditions in synthesizing new energetic bicyclic compounds and investigated other related parameters of the structures. Fused cyclic energetic materials, a unique class of large conjugate structures, which contain two or more rings, that share two atoms and the bond between the rings have been identified as promising contenders to traditional energetic materials (Scheme 7).²⁸ In 2020, Bayat and co-workers described the design and synthesis of energetic materials under mild and environmentally friendly conditions. A new strategy was used

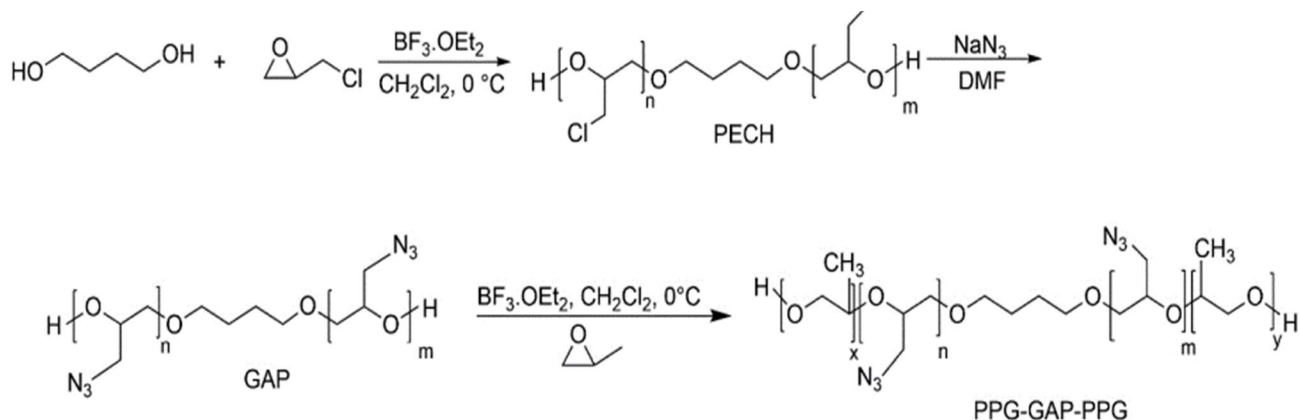


Scheme 6. Suzuki coupling using M-f-MWCNTs@chitosan-NHC-Pd

to synthesize energetic materials based on azides, which led to the creation of a new family of energetic materials (Scheme 9).²⁹



Scheme 7. Synthesis of FOX-7 (1,1-diamino-2,2-dinitroethene), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5-triazinane (RDX) and trinitrotoluene (TNT) according to the previously reported procedures

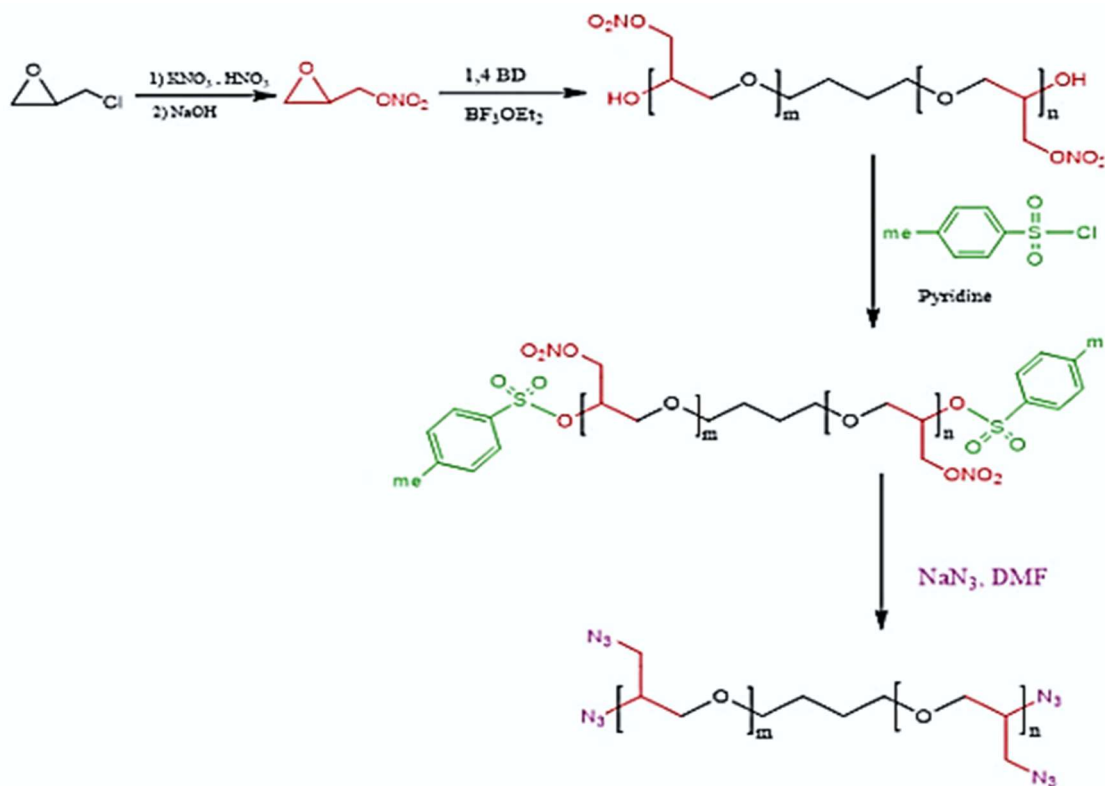


Scheme 9. Synthesis of the triblock copolymer PPG-GAP-PPG

Bayat et al succeeded in synthesizing new high-energy polymer compounds by using different catalysts under appropriate temperature conditions and investigated other parameters related to the structures. The newly synthesized high-energy materials have the capability of high loading capacity in solid propellants in war ammunition and have high mechanical and physical properties. (Scheme 10).³⁰

3. Conclusion

Due to the importance of chemistry in the synthesis of high-energy compounds, as well as the need of the military, oil, etc. industries for these high-energy compounds, it has caused many researchers to research and study in this field. With the increasing progress of chemical science and the provision of new methods that are compatible with the environment, as well as the easy access of other industries to this category of compounds, this is another reason for the attention of chemical scientists and other sciences to this very practical field.



Scheme 10. Synthesis of the polymer GAPA

Declaration of Interests

The author declares that she/he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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